

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to Compositions Containing Silver Halide

We, SOCIETE DE RECHERCHES SCIENTIFIQUES of 1, Place Puvis-de-Chavannes-LYON (Rhône), FRANCE, a French body corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions containing silver halide and to methods of preparing the same.

The silver ion has a restricted use in the field of general biology. This is probably due to a too ready acceptance of the conclusions drawn from the work of Raulin who demonstrated that infinitesimal traces of silver completely stop the development of *Sterigmatocystis nigra*, said conclusions heretofore being considered valid with respect to any living cell, both animal and vegetable. The work of Raulin was the starting point of attempts to use silver and its salts e.g. the nitrate, colloidal silver and the like, as antiseptics. In other words, in the field of biology, silver has been considered only as an antiseptic, astringent or caustic agent.

In a different art, namely that of organic synthesis, the catalytic role of silver is well known.

It is an object of the present invention to provide a silver-ion containing composition having a novel, bio-catalytic action which can be used both in the animal and vegetable biological arts.

According to one aspect of the invention there is provided a composition comprising an insoluble silver halide, a silver-sodium or silver-potassium thiosulphate complex and a silver thionate.

The invention also provides a method of preparing such a composition, which method

comprises the steps of (a) admixing a silver halide with a solution of a sodium or potassium thiosulphate to form a suspension, (b) thereafter admixing the suspension with a quantity of acid sodium or potassium sulphite and (c) concentrating the resulting mixture to form the desired composition, at least steps (a) and (b) being carried out in the dark or in red light.

Preferably, the silver halide used is silver chloride.

As regards the animal biological art, it has now been determined that local therapeutic applications of silver ion in the form of silver chloride followed by ultra-violet irradiations permit the accelerated regeneration of superficial and subjacent tissues, notably, osseous tissues.

As regards the vegetable biological art, laboratory and field tests have demonstrated that a slightly ionized silver salt, such as a silver halide, e.g. silver chloride, used under controlled conditions in small doses, will not only have no toxic effect but will, on the contrary, promote the development of crops and make it possible to obtain higher crop yields.

However, in both of the above mentioned uses, it is found that the rapid reduction of silver salt by light has the result that manipulations of the chloride or other halide alone encounter considerable difficulties.

Investigation has, however, shown that, in accordance with the present invention, the use of silver chloride is greatly facilitated when it is used in admixture with a silver complex which has been adapted for use in the same biological sense. Thus, the composition of the invention contains, in addition to the silver halide, a double silver and sodium (or potas-

[Price 4s. 6d.]

Price 25*s*

- sium) thiosulphate complex which has been treated with acid sodium (or potassium) sulphite, which results in the formation of thiocyanates. In general, the composition contains a mixture of two or more of the di-, tri-, tetra-, penta- and hexa-thionates, the specific thiocyanates present and the relative quantities thereof depending on the pH of the reaction mixture.
- The compositions of the invention have the important advantage that the silver halide contained therein is reduced much more slowly than normally, thus making its use for agricultural or medicinal purposes possible.
- A more detailed description of the preferred method by which the compositions of the invention can be prepared will now be given, by reference to the following Example 1.

EXAMPLE 1

Silver chloride was prepared, in darkness or in red light, by precipitation from a solution of AgNO_3 (1 kilo) using an excess of sodium chloride. After a washing with distilled water, the silver chloride was then added to a concentrated solution of sodium thiosulphate (1 kilo) to form a suspension of silver chloride in a solution of the double silver and sodium

thiosulphate salt. 200 ml. of acid sodium sulphite were added to the stirred suspension of silver chloride in the solution of silver and sodium thiosulphate. (The resulting mixture may then, if desired, be handled by daylight.) The mixture was concentrated *in vacuo* at a temperature in the range of from 70–80° C. During this concentration, a portion of the sulphite decomposed, evolving sulphur dioxide, whilst the other portion formed with the thiosulphate silver thiocyanates which ultimately ensured the stability of the product during the drying process, and, thereafter, during use of the composition.

In accordance with a preferred procedure, the concentrated mixture was pulverised and passed through a sieve. (These operations are preferably carried out in reduced or weak light or, better still, in a red light since handling of the powder under bright light may cause a superficial blueing.) The basic composition was preserved in brown bottles provided with a ground stopper and kept in a dark place.

The preferred composition thus formed constituted a ready-for-use base composition in accordance with the invention and is defined by the following composition:

55	—Silver chloride - - - - - —Double silver and sodium thiosulphate complex +silver thiocyanates - - - - - $(\text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O} +$ $\times \text{Ag}_2\text{S}_2\text{O}_6)$ —Sodium chloride - - - - -	14.3% by weight 72.6% by weight 13.1% by weight
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60 The composition had a silver titer of about 30%. The theoretical percentage of silver is 33.8% and the theoretical yield taking into account the water of crystallization is 1.874 kg. of composition starting with 1 kg. of AgNO_3 and 1 kg. of $\text{Na}_2\text{S}_2\text{O}_3$.

The compositions of the invention are used advantageously in association with compounds having a physiological or biological activity, such as steroids, e.g. a cholesterol and ergosterol. Due to the action of ultra-violet rays, ergosterol is "activated" to form D₃-vitamin; the silver composition accelerates this activation. Cholesterol is not transformed into an active vitamin D product but it does play the part of a filter absorbing noxious ultra-violet radiations having a wavelength of less than 2,500 Å. Although the addition to the composition of one or more sterols e.g. ergosterol; 7,8-dehydro-cholesterol; 7-hydroxy-cholesterol and 22-dehydrocholesterol, which are precursors of compounds with vitamin D action, is not compulsory, since certain precursory sterols exist normally in the irradiated organism, it is nevertheless very important in 85 the use of the silver composition for the reasons indicated above. An example of a composition containing such sterol additives is given below:

(a)	silver composition (Example 1)	10 g.	90
(b)	cholesterol	- - - - -	10 g.
(c)	ergosterol (or any other sterol which can be activated).	- - - - -	0.5 g.
(d)	fatty excipient, such as vaseline, q.s. for	- - - - -	100 g.

Examples of medicinal uses of the compositions of the invention are (a) the treatment of parodontosis, stomatitis, gingivitis and maxillo-facial diseases, (b) consolidation of dental implants, (c) consolidation of certain fractures, (d) treatment of acne and (e) beauty treatment.

Thus, for example, after massage of the gums, several decigrams of the above-exemplified composition (Example 2) are spread over the part to be treated, which is then subjected to an accurately localized ultra-violet irradiation. The time of irradiation varies from 1 to 3 minutes, depending on the progress of the treatment. This operation causes a degradation of the complex which can be detected by a blackening of the composition. The region treated is then protected by a wad of cotton for 5 to 10 minutes, during which time the irradiated product continues its action *in situ*.

Examples of the agricultural use of com-

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Results—The treatment of sugar-beet seeds with preparations having 5% of active ingredient produced constant results in an exceptionally dry year, as well as in an exceptionally humid year. During the very dry 1959 season, the increase in crop yield was of the order of 2 to 3 tons on 25 tons/hectare. During the very humid 1960 season, the increase in crop yield was 5 tons on 50 tons/hectare in two different tests. In the 1961 season, when climatic conditions were average, similar tests confirmed the above results.

C.
15 Plant tested—French (or string) beans
Time and place—1961: Barreuil (North of France)

In industrial farming producing beans for canning, plots of cultivated land were treated at the time of sowing with a powder having 2% of active ingredient and gave a bean yield which was 17% greater than that of a control plot.

WHAT WE CLAIM IS:—

- 25 1. A composition comprising an insoluble silver halide, a silver-sodium or silver-potassium thiosulphate complex and a silver thionate.
2. A composition according to Claim 1, wherein the silver halide is silver chloride.
- 30 3. A composition according to Claim 1 or 2, and further comprising one or more steroids.
4. A composition according to Claim 3, wherein said steroids are ergosterol and a cholesterol.

5. A composition according to any preceding claim and further comprising an inert diluent.

6. A composition substantially as described in any one of the foregoing Examples.

7. A method of preparing a composition as claimed in Claim 1, which method comprises the steps of (a) admixing a silver halide with a solution of a sodium or potassium thiosulphate to form a suspension, (b) thereafter admixing the suspension with a quantity of acid sodium or potassium sulphite and (c) concentrating the resulting mixture to form the desired composition, at least steps (a) and (b) being carried out in the dark or in red light.

8. A method according to Claim 7, wherein said mixture is concentrated *in vacuo* at a temperature in the range of from 70° to 80° C.

9. A method according to Claim 7 or 8, wherein the silver halide is silver chloride.

10. A method according to Claim 7, 8 or 9, wherein the concentrated mixture is dried and pulverized.

11. A method of preparing a composition as claimed in Claim 1, substantially as described in the foregoing Examples.

12. A composition whenever prepared by the method claimed in any one of Claims 7 to 11.

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